The Osmotic Data in Relation to Progressive Hydration.

By W. R. Bousfield, M.A., K.C.

(Communicated by Sir W. Ramsay, K.C.B., F.R.S. Received June 19,—
Read June 25, 1914.)

When a concentrated aqueous solution of an electrolyte is gradually diluted there is reason to believe that the amount of water in combination with the solute increases *pari passu* with the ionisation. This progressive hydration must be brought into the account in expressing the conductivity and the osmotic data (in which term we include freezing point and vapour pressure data) in terms of concentration. In a recent paper* it was shown that the latest determinations of the osmotic pressures of sucrose solutions by Morse and his co-workers could be simply and accurately expressed in terms of the progressive hydration of the solute. For the correlation of vapour pressure lowering with osmotic pressure, there was used the approximate relation obtained by the consideration of the equilibrium of a vertical column of liquid in contact with the pure solvent through a semi-permeable partition at the bottom and with the vapour of the solvent at the top, which contains as a factor ρ, the mean density of the solution. In the application of the expressions to concentrated solutions of electrolytes it soon became obvious that the presence of ρ, so far from helping the approximation, only threw it out, and the omission of ρ, or rather giving it a constant value unity, gave far more concordant results. In fact the errors introduced by the inclusion of ρ are much greater than the large experimental errors which occur in the measurement of the vapour of even concentrated solutions, whilst the errors when ρ is put equal to unity are considerably less than the experimental errors. The accurate measurement of the osmotic pressures of electrolytes has not yet been achieved, but the theoretical relation between osmotic pressure and vapour pressure forms the connecting link which enables us to express the vapour pressure data for electrolytes in terms of progressive hydration in the simple form

$$\delta p/p = i/(h-n)$$

without any density factor. It is, therefore, important to place the above result on a sound theoretical basis, since it appears to be of wide application in the study of electrolytes. The disappearance of the density factor is really a direct consequence of the relations developed by Callendar,† but his development is obscured by the fact that he uses the term "osmotic pressure" in a sense which permits its magnitude to vary from point to point of a solution of uniform concentration and temperature. He speaks, for instance, of "the assumption made by Lord Berkeley and Mr. Hartley that osmotic pressure varies with concentration only, which appears from their experiments to be approximately true for some solutions." It was pointed out in a recent communication* that this "assumption" is strictly true for all solutions, if we define osmotic pressure, in accordance with the requirements of the vapour pressure theory, as the liquid pressure under which the internal vapour pressure of the solution becomes equal to the vapour pressure of the pure solvent at the same temperature and under pressure of its own vapour only. From this definition the required relation can be deduced by considering the equilibrium of a small mass of solution of uniform concentration and pressure, instead of a column of solution of varying concentration and pressure. It may be noted that, at the suggestion of Sir W. Ramsay, we avoid the use of the term "hydrostatic pressure," and, in fact, the use of the term is out of place when deriving the relation from the consideration of a small mass of liquid which is mechanically compressed until its internal vapour pressure reaches a certain amount. We have to deal only with the liquid pressure at a point, which is a familiar conception. The idea of the internal vapour pressure at a point within a liquid is not so familiar, but it presents itself, for instance, in the conception of the equality of vapour pressures of ice and water in contact in a state of equilibrium. We may define the internal vapour pressure of a solution at a point as the pressure which would exist within a small sphere permeable only to the vapour of the solvent placed at the point. This conception brings us into line with the "vapour sieve piston" method by means of which Callendar established the relation

---

* 'Trans. Chem. Soc.,' vol. 105, p. 600 (1914).

† 'Roy. Soc. Proc.,' vol. 80, p. 466 (1908).

$$\mathrm{U}\,d\mathrm{P} = v\,dp,$$

where U is "the rate of diminution of volume of the solution at a pressure P per unit of mass of solvent abstracted," and v is the specific volume of the vapour at pressure p.

In Callendar's notation the value of U is

$$\mathrm{U} = \frac{1}{\rho} - \mathrm{C}\,d\left(\frac{1}{\rho}\right)\Big/ d\mathrm{C},$$

where C is the concentration in grammes of solute per gramme of solution. Examination of the densities of a number of aqueous solutions shows that we may with an inaccuracy of only about two or three parts per thousand take

$$\frac{1}{\rho} = \frac{1}{\rho \mathrm{w}} - \mathrm{BC},$$

---

* 'Roy. Soc. Proc.,' A, vol. 90, p. 41 (1914).

where ρ_W is the density of the solvent (water) and B is a constant. This gives us $d\left(\frac{1}{\rho}\right)/dC = -B$, and therefore

$$U = 1/\rho_W.$$

That is to say within this limit of accuracy U is simply the specific volume of water. The accuracy attained by taking this value of U is considerably beyond that of the experimental vapour pressure determinations which are available.*

For the utilisation of Callendar's equation we require to consider the effect of liquid pressure upon U. In the case of dilute solutions near the freezing point, the sensitiveness to pressure of the ice molecules present in large quantities disturbs the regularity of the osmotic pressures, as has been recently pointed out.† But in concentrated solutions this difficulty disappears owing to the destruction of ice molecules, and, since U is so closely related to the specific volume of water, we cannot be far wrong in taking for the small variation of U with liquid pressure an expression analogous to that which represents approximately the variation of the specific volume of water with pressure.

Let p_0 = vapour pressure of the solution under pressure of its own vapour only,
p_W = vapour pressure of water under pressure of its own vapour only,
$\delta p = p_W - p_0$, the vapour pressure lowering of the solution
P = liquid pressure of the solution,
U_0 = value of U when $P = p_0$.

Then we may say $$U = U_0[1-\beta(P-p_0)],$$

or, since the magnitude of β is of the order 0·00005, we may for the purpose of integration conveniently take

$$U = U_0[1+\beta(P-p_0)]^{-1}.$$

We may also, within the desired limits of accuracy, take for the relation between the pressure and specific volume of saturated water vapour

$$v = R'T/p.$$

Substituting these values for U and v in the equation

$$U\,dP = v\,dp,$$

---

* For instance, in the extreme case of 40-per-cent. lithium chloride solution, the value of U is 0·996, which only differs from the value of U for an "infinitely dilute" solution by 1 part in 200. The error in the vapour pressure lowering determined experimentally is not less than 1 in 100.

† 'Roy. Soc. Proc.,' A, vol. 90, p. 45 (1914).

and integrating at constant temperature, we get

$$\frac{U_O}{\beta}\log[1+\beta(P-p_O)] = R'T\log(p/p_O).$$

The integration constant is obtained from the consideration that the liquid pressure in the solution when under pressure of its own vapour only is p_O, that is to say, when $p=p_O$ we must have also $P=p_O$. The above equation expresses the relation between liquid pressure P and internal vapour pressure p. As the liquid is compressed by varying pressures P the internal vapour pressure p is changed in accordance with the above expression. But it is essential to clearness of ideas not to regard any value of P as "osmotic pressure" except the particular value which P must have in order to make $p=p_W$. Thus we get for the osmotic pressure in accordance with our definition

$$\log[1+\beta(P-p_O)] = \frac{\beta R'T}{U_O}\log(p_W/p_O),$$

where P now stands for the osmotic pressure of the solution at absolute temperature T.

Putting $\delta p=p_W-p_O$, expanding the logarithms, neglecting small quantities of the second order and neglecting also p_O in comparison with P on the left-hand side we obtain the equation

$$\frac{P}{R'T} = \frac{1}{U_O}\cdot\frac{\delta p}{p_W},$$

which has already been obtained by Callendar, Porter and others. The point of the deduction set out above is that the expression is deduced from the strict definition of osmotic pressure, which does not permit us to regard osmotic pressure as varying with "hydrostatic pressure."

Since within the limits of experimental error of vapour pressure determinations we can put $U_O=1$, the expressions formerly given for the osmotic data in terms of progressive hydration* can now be put in the simpler and yet more accurate form,

$$\frac{P}{R'T} = \frac{\Delta}{F'} = \frac{\delta p}{p} = \frac{i}{h-n}.$$

Here P is the osmotic pressure expressed in atmospheres, Δ is the freezing point depression of the solution, $\delta p/p$ is the ratio of the vapour pressure lowering to the vapour pressure of water at the same temperature, h is the total number of molecules of water to one molecule of solute, n is the number of molecules of water in combination with one molecule of the solute, and i is the ionisation factor, the best values of the constants being $R'=4{\cdot}557$ and $F'=103{\cdot}6$.

---

* 'Trans. Chem. Soc.,' vol. 105, p. 609 (1914).

As an illustration of the practical value of the relations thus formulated we may refer to a paper written concurrently with the present communication,* in which it is shown by their use that the dilution law $\alpha^2/(1-\alpha)=K(h-n)^{\frac{3}{2}}$ is valid for the chlorides of lithium, sodium and potassium both in dilute and in concentrated solutions and that it is in conformity with the requirements of the law of mass action. There is reason to believe that the simple relation $\delta p/p=i/(h-n)$ which it is the purpose of the present communication to establish is even more accurate than the approximations by which it is reached would lead us to expect, and that the small inaccuracies introduced by the approximations practically cancel one another, except in the region of dilute solutions near the freezing point, in which the idiosyncrasies of water are so marked. But here the relation is never in practice required, since the values of δp are so small as to be incapable of direct measurement.

On the Origin of the Electron Emission from Glowing Solids.

By Frank Horton, Sc.D.

(Communicated by Prof. Sir J. J. Thomson, O.M., F.R.S. Received May 14,—Read June 25, 1914.)

(Abstract.)

The electron emission from Nernst filaments has been measured under different conditions and the following results have been obtained :—

1. The electron emission from a filament heated by an alternating current is of the same magnitude as that obtained when the filament is heated by a continuous current to the same temperature.

2. The electron emission from a Nernst filament at a given temperature is the same when heated by conducting an electric current as when heated by a glowing metal wire passing through it.

3. The electron emission from a Nernst filament heated in the usual manner is the same as that given by the material of the filament when powdered and heated upon platinum.

These results show that the action of an oxide cathode does not depend

---

* 'Trans. Chem. Soc.,' vol. 105, p. 1809 (1914).